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METHOD AND DEVICE FOR CONTINUOUS TREATMENT OF COPPER SULPHIDE CONTAINING ORE BY BIOLOGICAL LEACHING

The present invention relates to a method and a device for continuously treating copper sulphide containing ores with a view to recovering said copper.

Numerous metals, such as copper, silver, gold or palladium, exist in nature in association with other ores. In order to recover them, many methods have been described in the prior state of the art, consisting, during a first step of biological leaching, in causing to act on ores bacteria of diverse type which ensure destruction of the sulphur-containing matrix imprisoning a determined metal, by dissolution of this matrix, this having the effect of dissolving the metal in question. In a second step of treatment, the metal contained in this solution is recovered by intervening on said solution, particularly by the chemical and/or electrochemical route.

For example, US-A-4 571 387 proposed a method of leaching sulphurous copper ores, for example chalcopyrite ($CuFeS_2$), in which the copper ores are placed in contact with strains of the bacterium *Thiobacillus ferrooxydans* capable of oxidizing the sulphides, in an aqueous acid solution, and Cu^{2+} ions as well as sulphur and sulphate or sulphuric acid form by oxidation of the ore. The Cu^{2+} ions may then be treated by a liquid/liquid extraction. A similar method is described in U.S. Patent No. 4 729 788 which describes the use of

thermophilic bacteria of *Sulfolobus* type to ensure leaching of sulphurous gold and silver ores.

U.S. Patent 5 919 674 also proposed a method for carrying out a part of the first step of continuous biological leaching of copper ores by means of a bacterium, particularly of Sulfolubus type. However, it appears that such a method does not easily lend itself to implementation from the industrial standpoint.

The present invention has for its object to propose a method aiming at recovering the copper contained in sulphur containing ores, comprising a step of continuous biological leaching, and this by using a novel thermophilic bacterial culture, of Sulfolobus type.

The present invention thus has for its object a method for treating copper sulphide containing ore, comprising a step of biological leaching whereby the minerals are subjected in reactors in cascade arrangement, wherein the temperature is maintained between 75°C and 85°C, to the action of a bacterial culture, which comprises a thermophilic bacterium of the Sulfolobus type, leading to solution of the copper, characterized in that, during said biological leaching step:

- the treatment is uninterrupted,

- the medium containing the bacterial culture is continuously mechanically agitated to ensure oxygenation thereof and suspension of the solid elements,

- the solid mass proportion of the culture medium is maintained above 10%.

The bacterial culture used is a novel

culture which is in fact a mixture of bacteria capable of catalyzing oxidation of the sulphides and which presents an optimal growth temperature included between 75°C and 85°C. This bacterial culture has been progressively adapted in order to improve its tolerance to copper. Such an adaptation was made by successive transplantings on a substrate of chalcopyrite, in the course of which the concentrations of copper in solution were progressively and artificially increased. Such an adaptation made it possible to render these bacteria capable of developing in media of which the concentration of copper is of the order of 50 g/l.

The sulphur containing minerals are preferably furnished to the culture medium in the form of a sulphur containing concentrate presenting a granulometry d80 less than one hundred micrometers.

According to the invention, a pH included between 1.2 and 1.6 is maintained in the biological leaching reactors, particularly by addition of calcium carbonate.

The step of biological leaching will be followed by a second step during which, in a first phase the pulp issuing from the biological leaching reactors is admitted in precipitation reactors in which the iron is eliminated by provoking a precipitation of jarosite, by addition of calcite, and the solution is maintained at a pH less than 3, and the neutralized pulp is admitted in a decanter and a part of the solids is made to recirculate at the head of the precipitation reactors.

In a second phase of this form of embodiment, the liquid issuing from the decanter is admitted in

neutralization reactors in which a pH of the order of 3.5 is maintained, particularly by an addition of calcite, so as to entrain only a minimum of copper, and one proceeds with filtration of the pulp obtained.

In a third phase of this form of embodiment, the aqueous phase of the liquid coming from filtration is admitted in a unit of extraction by organic solvent in which it is subjected to the action of an extracting product, so as to transfer the copper of the aqueous phase into the organic phase, the operational conditions are modified so as to transfer the copper of the organic phase of the extracting product into a pure aqueous phase.

In a variant embodiment of the invention, the outlet of the extraction unit will be placed in communication with the inlet of the precipitation reactors, so as to cause part of the raffinate collected at this outlet to be recirculated by causing it to traverse said reactors again with a high flowrate with respect to the flowrate of the pulp coming from the biological leaching reactors, so as to provoke a dilution of the aqueous solution subjected to extraction, up to a concentration of copper of the order of about 10 g/l, i.e. up to a value corresponding to the possible extraction of the copper in an extraction unit.

The present invention also has for an object a device for continuously treating copper sulphide containing ores of the type comprising biological leaching means in which the minerals are subjected to the action of a bacterial culture leading to the solution of the copper, at

a high concentration, of the order of 40 g/l, followed by the means for precipitating the iron contained in this solution, by addition of calcium carbonate, followed by means of extraction by organic solvent, characterized in that the outlet of the means of extraction by solvent is in communication with the inlet of the precipitation means, so as to cause a part of the raffinate collected at that outlet to recirculate, by causing it to traverse the precipitation means again with a high flowrate with respect to the flowrate of the solution at the outlet of the biological leaching means, so as to provoke a dilution of the aqueous solution subjected to extraction, up to a concentration of copper less than that existing at the outlet of the biological leaching means and preferably of the order of 10 g/l.

According to the invention, the reactors used during the biological leaching step comprise means making it possible to channel the gaseous fluid which traverses them towards condensation means.

A form of embodiment of the present invention will be described hereinafter, by way of non-limiting example, with reference to the accompanying drawing, in which:

The single Figure schematically shows the different steps of the method according to the invention.

According to the invention, the bacteria are placed in culture in stirred and aerated reactors 1 which are continuously supplied with sulphur containing minerals put in the state of pulp. This pulp is transferred from one reactor to the other by overflow. The culture medium, which is constituted by the sulphur containing minerals and the bacterial culture,

is supplied with nutritive elements which are indispensable for the growth of the micro-organisms of the culture, whose concentrations have been optimalized in order to allow a good growth thereof.

Of course, the reactors may be arranged in a configuration other than in cascade, and the transfer of the pulp from one reactor to the other may be effected by means other than an overflow, and in particular by pumping means, whether they be mechanical or with carrier gas effect (so-called "Air lift" systems).

Furthermore, it is known from the prior state of the art that the biological constitution of the external membranes of thermophilic bacteria is such that these bacteria prove to be relatively fragile as to the physical stresses of attrition that they are likely to have to undergo and which are associated with the presence of solid particles in solution when the rates of solid (expressed in percentage by mass) are greater than 1%.

It is also known that these bacteria are sensitive to the shear stresses that they undergo, particularly when they are in the presence of mechanical stirring means.

According to the invention, the bacterial culture has also been subjected to an adaptation intended to increase the percentage of rate of solid used. To that end, the rates of solid of the solution placed in the presence of the bacterial culture have been increased, by successive stages, and the bacteria have been able to tolerate

mass solid rates of the order of 10% to 15%.

It is known that the implementation of such a process necessitates an oxygenation of the culture medium which, in the present case, will be ensured by an injection of air at the bottom of the vat. In the event, during the process, of the concentration of dissolved oxygen proving to be insufficient, the injected air might be enriched with pure oxygen so as to improve the transfer of the oxygen towards the solution and thus promote oxidation of the sulphur containing mineral substrate. This injected air may also be enriched with carbon dioxide which constitutes the carbon substrate of this type of bacteria.

The stirring to which the bacterial culture is subjected during reaction is a mechanical stirring which is obtained with the aid of an electric motor connected to a vertical rotating shaft provided with so-called "mobile stirring" elements. A first mobile stirring element called "turbine" is disposed in low position of the shaft and is constituted in known manner by a disc of which the lower face comprises multiple radial plates which, during rotation of the disc, ensure an action of shear provoking dispersion of the air injected in the bacterial culture. The second mobile element is disposed in the upper part of the reactor and is constituted by a propeller. This mobile element presents good pumping characteristics and thus promotes the mixture and homogenization of the culture medium. The person skilled in the art will be able to optimalize such stirring means so as to ensure an optimal development of the bacterial culture.

It is ascertained that, surprizingly, the thermophilic bacterial culture used was thus in a position to withstand relatively energetic stirring means and high shear effect.

Furthermore, as a function of the nature of the mineral substrate used, steps will be taken to maintain the pH of the culture medium at a value preferably included between 1.2 and 1.6, and this by well mastering the various operational conditions. However, it will be noted that the value of the pH may be regulated, particularly in the event of drop of the latter, at values less than 1.2, by the controlled addition of calcium carbonate, of which the dissolution will, furthermore, contribute carbon dioxide.

In order to reduce the losses of water due to evaporation in the reactors, which may be translated by a non-controlled increase in the concentration of the elements in solution capable of disturbing the development of the culture, closed reactors will be used in which the emerging air flow will traverse condensation means. If such losses are not reduced sufficiently in this way, either a punctual addition of water can be made or a supply of nutritive solution without addition of concentrate can be effected, and this for a period of time adapted to the loss of water ascertained.

In a particularly interesting form of embodiment of the invention, a condensation system may be used intended to orientate the flow of air in order to position means for on-line analysis of the gases emerging from the reactors. Such means may thus make it possible to obtain, in real time, information on the state of the

bacterial culture and thus to ensure complete follow-up of the treatment device.

The first step of the method of treatment according to the invention, namely the step of biological leaching, being terminated, a pulp is obtained at the outlet of the reactors which contains, in addition to the copper in solution that it is desired to isolate, at a concentration of about 40 g/l, diverse chemical products which are either dissolved in the liquid phase, or in solid form and in particular the residue of non-degraded ore, gypsum and ferric iron hydroxides.

The following steps of the method will therefore consist firstly, during an intermediate step, in separating these various components in order to extract, during a subsequent step of electrolysis, the metal copper from the purified solution.

In the course of this intermediate step, the iron will firstly be eliminated. To that end, the pulp issuing from the bank 1 of biological leaching reactors is admitted in a bank 5 of a plurality of reactors in which calcite is introduced at 6. In effect, it is known that the iron which is mainly available in its oxidized form Fe^{+3} is neutralized by the calcite which provokes a precipitation of compounds of jarosite type (i.e. a precipitate containing iron, sulphate, and a counter cation that may be H_3O^+, Na^+, K^+, or NH_4^+) of hydroxides and of gypsum.

Now, it is known that the precipitation of jarosite, which is particularly interesting, since, on the one hand, it allows a lesser consumption of calcite and, on the other hand,

the solid precipitates obtained present facilities of filtration much more interesting than the compounds of hydroxide type, is largely promoted by a relatively high temperature (which is the case of the pulp issuing from biological leaching) and that this type of precipitate is stable at low pH's (less than 3). The pH will therefore be monitored in the reactors in order to maintain it at a value less than 2.8, and this by monitoring the addition of calcite.

The installation will comprise, downstream of bank 5, in the reactors of which the jarosite precipitates, a decanter 7 which presents an outlet 8 connected to the inlet 4 of the bank 5 and which makes it possible to cause a part of the solids to recirculate "at the head of neutralization" so that, by germination, the growth of crystals will be promoted. In this way, not only the speeds of growth of the minerals, but also the characteristic of good capacity for filtration of the solids are thus improved. Here it is question of parameters which are particularly interesting in an industrial installation, as they intervene directly on the dimensioning and therefore on the cost thereof.

The rest of the iron in solution is then eliminated, in the form of hydroxides, by means of a bank 11 constituted by neutralization reactors, disposed downstream of the decanter 7, in which a pH of 3.5 is maintained by addition of calcite at 12, so as to entrain by coprecipitation only a minimum of copper. A band filter system 13 collects the pulp at the outlet 10 of the bank 11 and makes it possible to ensure a solid/liquid separation.

Such a filtration system is constituted in known manner by a band on which the pulp is admitted and which is stretched between drums which ensure its drive in rotation. Suction means are applied through the band and a cake of increasing thickness is obtained during the displacement thereof, which is extracted at 14 after it has undergone one or more washing operations.

This solution is then sent in 16 in a unit 17 for extraction by organic solvent. It is known that such a unit is formed by a plurality of mixers/decanters in which is introduced the solution to be treated, a mixture constituted by specific extracting products and a diluent. By reason of the different affinity of the copper for the aqueous phase and for the organic phase which depends on the operational conditions, it is possible (under determined operational conditions) to transfer the copper in the organic phase then, by changing the operational conditions (contacting of the organic phase with an aqueous solution rich in sulphuric acid), to return the copper in a pure aqueous solution so as to be able then to ensure recovery of the metal copper by electrolysis. During this operation, the impurities that may pollute the cathodes during electrolysis have been eliminated.

A reactant marketed by the firm HENKEL under the Trademark "LIX" will preferably be used as extracting product.

However, it will be noted that the selective extraction of the copper with the extracting products being a

chemical reaction of exchanges between proton and cation, the result is that, for each cuprous ion extracted, two protons are released by the extracting product. This production of acid brings about a decrease of the pH in the aqueous phase (raffinate). Now, by reason of the considerable rates of solid of the pulp issuing from the biological leaching step, the quantity of copper in solution is high and the mass of acid thus generated during the extraction induces a decrease in the pH to values which hinder extraction, and even render it impossible. It is therefore necessary to take steps for the pH to be maintained at a value compatible with that allowing extraction.

Furthermore, it has been ascertained that the first step of the method, namely the biological leaching step, delivers a pulp presenting a considerable concentration of copper, close to 40 g/l, and it is known that the operation of extraction makes it possible to extract only concentrations of copper of the order of 10 g/l at these pH values.

Of course, it might be possible to work at less high solid rates during the biological leaching step, but such treatment means would in that case impose, for an identical quantity of copper produced, that biological leaching reactors of much greater volume be available, which would have the drawback of increasing the complexity, the dimensions and the cost of the installation.

A form of embodiment of the invention, which represents a first solution allowing these drawbacks to be overcome, will be described hereinafter with reference to the single Figure.

In this form of embodiment, the outlet 19 of the extraction unit 17 is placed in communication with

the inlet 4 of the bank 5, so as to cause a part of the raffinate collected at that outlet 19 to be recirculated by causing it to traverse the bank 5 again. In this way, upon passage therein, the addition of calcite, which is effected at 6, has the effect of increasing the pH of the solution, so as to compensate the decrease thereof due to the emission of the H^+ ions during extraction. Furthermore, by adjusting the flowrate of recirculation Q2, which is high with respect to the flowrate Q1 of the pulp admitted in the bank 5 coming from the biological leaching bank 1, a dilution of the aqueous solution subjected to extraction is provoked, to a concentration of the order of about 10 g/l, i.e. to a value corresponding to the possible extraction in an extraction unit 17.

This form of embodiment is particularly interesting insofar as it ensures extraction of the copper from a pulp with a high concentration of copper by using one single extraction unit and without additional use of devices intended to raise the pH.

In a second form of embodiment of the invention, recirculation of a part of the raffinate will not be effected, and successive means will be arranged making it possible, on the one hand, to raise the pH of the solution after extraction, and, on the other hand, to extract this solution of modified pH, until the 40 g/l of copper contained in the starting solution have been extracted.

It will then remain to carry out the last step of the method according to the invention during which, in an electrolytic cell 20,

electrolysis of the raffinate recuperated at the end of extraction will be effected in order to recuperate the metal copper.